Effects of CO_2 on synthesis of isobutene and isobutane from $CO_2/CO/H_2$ reactant mixtures over zirconia-based catalysts

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Abstract

The effects of CO_2 on the selective formation of i-C_4 hydrocarbons (isobutene and isobutane) from $CO_2/CO/H_2$ reactant mixtures were studied. Three ZrO_2-based catalysts including unmodified ZrO_2, 8.6%Y_2O_3-ZrO_2, and 15.3%Al_2O_3-0.5%K_2O-ZrO_2, were used in this study. The catalysts were characterized by N_2 adsorption, X-ray diffraction (XRD), Raman, spectra, temperature-programmed desorption (TPD) of ammonia and carbon dioxide, and temperature-programmed reduction (TPR). The influences of CO_2 on the catalytic performances of the catalysts were investigated by varying the content of CO_2 in the feed up to 20%. It was found that the addition of CO_2 in the synthesis gas (CO/H_2) significantly reduced the net formation of CO_2, but did not affect the formation of hydrocarbons. For the distribution of hydrocarbons, the selectivity to i-C_4 in total hydrocarbons decreased with increasing the content of CO_2 in the feed, while the selectivities to C_1–C_3 hydrocarbons increased. However, the i-C_4 selectivities in all products were enhanced significantly because of the inhibition of CO_2 formation with CO_2 adding in the feed. The predominant products in CO_2 hydrogenation on the ZrO_2-based catalysts were CO and H_2O at 648–723 K, indicating that the ZrO_2-based catalysts were not active in the reactions towards hydrocarbons from CO_2/H_2. A 5–6% yield of i-C_4 hydrocarbons with ∼62% selectivity in the products was achieved on 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst at 8–9% CO conversion with 20% CO_2 adding in the feed at 698 K. The yield of CO_2 was only 0.5% (∼5% CO_2 selectivity in the products). Our results would suggest one potential way of using the recycle of CO_2 formed to selectively synthesize i-C_4 hydrocarbons from coal or natural gas-derived syngas (CO + H_2) with high carbon efficiency (with free or very low CO_2 emission).
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1. Introduction

Isobutene and isobutane (i-C_4 hydrocarbons) are important starting materials for many industrial synthesis products, such as, diisobutylene, trimers, isooctane, butyl rubber, and other polymers, etc. Presently they are primarily produced by extracting from C_4 hydrocarbons stream of petroleum cracking processes [1]. However, these traditional supplies of isobutene and isobutane are insufficient to meet the continuously expanded demands. In addition, the continuously rising high price of petroleum worldwide in recent years would make the traditional supplies be more and more expensive. Therefore, it is very urgent to search for alternative supplies of isobutene and isobutane.

Isosynthesis reaction represents one potential way for producing isobutene and isobutane, which has been referred to as the reaction that selectively converts coal or natural gas-derived syngas (CO + H_2) to iso-C_4 hydrocarbons (most of i-C_4 hydrocarbons is isobutene in the isosynthesis). It has the advantage over traditional petroleum cracking processes because of the enormous storages of coal and natural gas on the earth. Thorium dioxide (ThO_2) and zirconium dioxide (ZrO_2) have been recognized to be the most active and selective catalysts for isosynthesis [2,3]. Recent research has mostly focused on ZrO_2-based catalysts because of their absence of radioactivity and high selectivities to isobutene [4–12].

However, isosynthesis reaction suffers from the low carbon efficiency because of the large proportion of CO_2 existed in the products. The selectivities to CO_2 were mostly in the range 40–60% under the typical isosynthesis temperatures (673–698 K),

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as reported in the literatures [6–10,13–17]. In Maruya's experiments, the CO_2 selectivities varied from 60 to 80% [4,5,18–22]. This resulted in very low i-C_4 selectivities in the products (<40%). In addition, CO_2 is known to be the main source of green house gases that warm up the atmosphere [23]. Therefore, it is not environmentally friendly if so much CO_2 were released into the atmosphere. With the continuously increasing environmental concerns and stringent regulations, it is very critical to reduce the production of CO_2 during the isosynthesis reaction.

The formation of CO_2 in the CO hydrogenation is mainly from the known water-gas shift (WGS) reactions ($CO + H_2O \leftrightarrows CO_2 + H_2$). Fe-based catalysts are known to be active for these CO_2-forming reactions [24]. In traditional high-pressure isosynthesis reactions, stainless-steel tubes were normally used [6–17]. That leads to high CO_2 selectivities and low selectivities to i-C_4 hydrocarbons. We have designed a quartz-lined stainless-steel tubular reactor to prevent reactants from contacting with the stainless-steel walls [25]. By using the specially designed reactor, the selectivity to CO_2 was reduced from 46.8 to 37.7% on the same unmodified ZrO_2 catalyst. We also found that the selectivities to CO_2 varied with the catalysts possessing different acid–base and redox properties [11,12]. But the effects were not remarkable.

WGS reactions are favorable in thermodynamics ($\Delta_r G < 0$) at typical isosynthesis reaction temperatures (648–723 K) [24]. So the WGS reactions are always close to equilibrium during the isosynthesis reactions. It is well known that a small change in concentrations of the reactants or products when the reaction approaches equilibrium will largely drive the reaction deviating from the original equilibrium position. Therefore, an addition of CO_2 to syn-gas (CO/H_2) would enhance the reverse WGS reaction, and hence could reduce the conversion of CO to CO_2. The effects of CO_2 addition on the Fischer–Tropsch synthesis (FTS) and alcohols synthesis from CO/H_2 have been investigated [26–30]. However, to the best of our knowledge, there is still no report on the isosynthesis reaction with the introduction of CO_2 in the feed.

Here, we report the effects of CO_2 on the synthesis of i-C_4 hydrocarbons from $CO_2/CO/H_2$ reactant mixtures. Three typical ZrO_2-based catalysts that have remarkably different surface acid–base and redox properties were selected in order to examine the effects of these surface properties on i-C_4 synthesis from $CO_2/CO/H_2$. The roles of acid–base and redox properties of catalysts on the isosynthesis reaction (with CO/H_2 as reactants) have been widely investigated and suggested [6–22]. However, the catalysts themselves and subsequently their catalytic performances in the synthesis of i-C_4 could be affected with CO_2 present in the reactant mixture ($CO_2/CO/H_2$) because CO_2 is known to be an acidic gas and also oxidizing compound [29,31]. Therefore, the effects of acid–base and redox properties of catalysts on the synthesis of i-C_4 with CO_2 present in the feed ($CO_2/CO/H_2$) could be different from that without CO_2 present (CO/H_2). In this study, the roles of CO_2 in the reactant mixtures on the isosynthesis reactions were addressed by comparing the $CO_2/CO/H_2$ reaction results with the CO/H_2, and also CO_2/H_2 reaction results on the identical catalysts. The possibility of using CO_2 recycle when CO/H_2 are used on ZrO_2-based isosynthesis catalysts is proposed based on the obtained experimental results and thermodynamics theoretical calculations.

2. Experimental

2.1. Catalyst preparation

The preparation of unmodified ZrO_2, 8.6%Y_2O_3-ZrO_2, and 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalysts have been described in detail in our previously published papers [11,12]. Briefly, ZrO_2 was prepared by precipitation of a $ZrOCl_2$ solution with an ammonium solution (2.5 wt%). After thorough washing with deionized water, the precipitate was dried at 378 K for 24 h and then calcined at 823 K for 3 h in air. 8.6%Y_2O_3-ZrO_2 mixed oxide was synthesized by coprecipitation of a mixed solution $ZrOCl_2$ and yttrium nitrate salt, with ammonium solution (2.5 wt%), and then the above procedure was followed. 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst was prepared by physically mixing the prepared ZrO_2 with Al_2O_3 and KOH at a certain ratio. The mixture was then calcined in air at 823 K for 1.5 h.

2.2. Catalyst characterization

Powder X-ray diffraction data was recorded on a Brüker D8 advance powder diffractometer using nickel-filtered Cu-Kα radiation. N_2 adsorption/desorption isotherms at 77 K were measured with a Micromeritics ASAP 2010C analyzer. Prior to measurements, the samples were degassed in vacuum at 473 K for 6 h.

The acidic and basic properties of the catalysts were measured by temperature-programmed desorption (TPD) of ammonia and carbon dioxide, respectively, in a flow-type apparatus at atmospheric pressure [12]. Temperature-programmed reduction (TPR) studies of catalysts were carried out in a conventional system equipped with a thermal conductivity detector (TCD) [12]. A flow of 5% H_2/Ar (20 ml/min) and a heating rate of 10 K/min were used for the TPR measurements.

2.3. Measurement of catalytic activity

All the experiments were carried out in one specially designed high-pressure flow fixed-bed reactor at 5.0 MPa, 648–723 K, and 650 h^{-1} [12,25]. One gram of catalyst (20–40 mesh) was used for each experiment. The reactant and effluent streams were analyzed with two on-line gas chromatographs. One equipped with TCD was used to separate CO, CH_4, CO_2, H_2O, CH_3OH, and CH_3OCH_3 through a GDX-101 column, and another equipped with FID and a 30 m × 0.53 mm Al_2O_3 capillary column was applied to separate hydrocarbons. The calculations of CO_2 selectivity and yield were based on the net formation amount of CO_2 in the reaction, which was obtained by subtracting the CO_2 quantity in the reactant stream from that in the products. In all

Table 1
BET surface areas, pore volumes, amounts of acidic and basic sites, and H_2 consumption amounts in TPR of the catalysts

Catalyst	S_{BET} (m^2/g)	Pore volume (cm^3/g)[a]	Crystal phase	Amount of acidic sites ($\mu mol/g$)[b]	Amount of basic sites ($\mu mol/g$)[c]	H_2 consumption in TPR ($\mu mol/g$)
ZrO_2	55	0.212	M^d	41.5	81.0	7.2
8.6%Y_2O_3-ZrO_2	120	0.157	C, T^e	42.8	61.3	62.4
15.3%Al_2O_3-0.5%K_2O-ZrO_2	75	0.222	M	45.1	138.3	9.8

[a] BJH desorption cumulative pore volume of pores in the range 1.7–300 nm.
[b] Measured by NH_3-TPD.
[c] Measured by CO_2-TPD.
[d] Monoclinic phase.
[e] Cubic and tetragonal mixed phases.

experiments the mass balances in carbon and oxygen were within ±2%.

3. Results and discussion

3.1. Characterization results

The BET surface areas, pore volumes, amounts of acidic and basic sites, and H_2 consumption amounts in TPR of the ZrO_2-based catalysts are summarized briefly in Table 1. Most of the detailed characterizations of these catalysts have been discussed previously [11,12]. Among the three catalysts, 8.6%Y_2O_3-ZrO_2 has the highest BET surface area but the lowest pore volume. X-ray diffraction (XRD) patterns showed that monoclinic phase was the dominating crystal phase for unmodified ZrO_2 or 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst. Raman spectrum showed that 8.6%Y_2O_3-ZrO_2 exhibited mixed crystal phases with a cubic phase and a tetragonal phase coexisted [12].

ZrO_2 has been well known as a bifunctional catalyst with both weakly acidic and basic sites [32]. No significant differences were observed on the desorption temperatures of NH_3 and CO_2 between the 15.3%Al_2O_3-0.5%K_2O-ZrO_2 or 8.6%Y_2O_3-ZrO_2 catalyst and pure ZrO_2 [11,12]. All the catalysts had very similar amounts of acidic sites. However, the amounts of basic sites markedly varied with the types of dopants added to ZrO_2. As shown in Table 1, the quantities of basic sites follow the order: 15.3%Al_2O_3-0.5%K_2O-ZrO_2 > Z-ZrO_2 > 8.6%Y_2O_3-ZrO_2. H_2-TPR results showed that the reduction behavior of the 8.6%Y_2O_3-ZrO_2 catalyst was remarkably improved in comparison to that of unmodified ZrO_2 catalyst. This improvement is suggested to be related to the increased mobility of lattice oxygen of the catalyst [33]. The addition of Al_2O_3 and K_2O to ZrO_2 by mechanical mixing hardly affected the reduction behavior of ZrO_2.

3.2. Effects of the addition of 5% CO_2 to synthesis gas on isosynthesis

The effects of CO_2 addition on isosynthesis reaction were examined by comparing the catalytic activities and selectivities from the syngas (CO/H_2 = 1/1) with that from CO_2/CO/H_2 on the same catalyst under the same conditions. Three catalysts, ZrO_2, 8.6%Y_2O_3-ZrO_2, and 15.3%Al_2O_3-0.5%K_2O-ZrO_2,

were used to investigate if the effects of CO_2 addition would depend on the surface properties (such as acid–base and redox) of the catalysts. As reported previously, 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst had the highest i-C_4 selectivity but the lowest selectivity to CO_2 among the three catalysts [11,12], while 8.6%Y_2O_3-ZrO_2 catalyst was most active for the formation of CO_2 from CO hydrogenation.

The CO conversion, yields of hydrocarbons and CO_2, and i-C_4 selectivity in total hydrocarbons are shown as a function of temperature on ZrO_2 catalyst in the two reactant mixtures (CO/H_2 and CO_2/CO/H_2, CO_2: 5%) in Fig. 1. The ratios of CO to H_2 were 1/1, and the total pressures were 5.0 MPa for both reactant mixtures. The conversions of CO, yields of hydrocarbons and CO_2 all increased with increasing temperature under both reaction atmospheres (CO/H_2 and CO_2/CO/H_2). It can be seen that the addition of 5% CO_2 to the synthesis gas (CO/H_2) decreased the conversions of CO, and CO_2 yields at all temperatures, but the yields of hydrocarbons were enhanced slightly. The results indicate that the presence of CO_2 in the feed diminishes the net formation amounts of CO_2 during the reactions by increasing the rates of reverse WGS reaction and inhibiting the rates of CO_2 formation reactions. The increase in the rates of reverse WGS reaction with the addition of CO_2
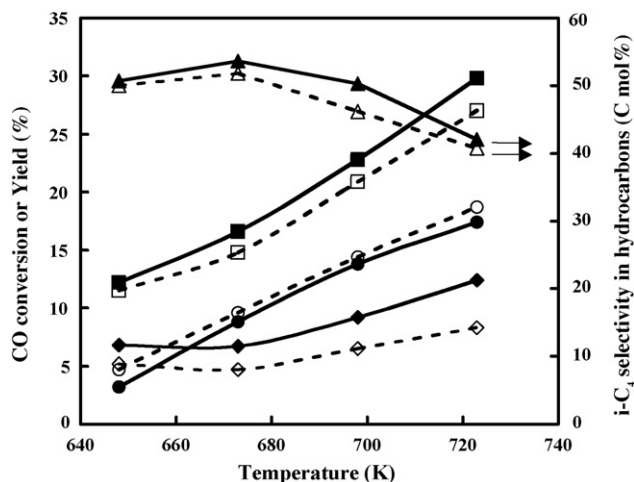
Fig. 1. CO conversion (■, □), yield of hydrocarbons (●, ○), CO_2 yield (◆, ◇), and i-C_4 selectivity in total hydrocarbons (▲, △) as a function of temperature on ZrO_2 catalyst from CO/H_2 (filled symbols, CO/H_2 = 1/1) or CO_2/CO/H_2 (open symbols, CO/H_2 = 1/1, CO_2: 5%) at a total pressure of 5.0 MPa and 650 h^{-1}.

Table 2
Comparison of H_2 conversions from CO/H_2 and $CO_2/CO/H_2$ reactions in the quartz-lined stainless-steel tubular reactor[a]

Catalyst	Feed gas	H_2 conversion (%)			
		648 K	673 K	698 K	723 K
ZrO_2	CO/H_2[b]	4.5	14.3	20.3	25.4
	$CO_2/CO/H_2$[c]	9.0	17.2	25.8	34.6
$15.3\%Al_2O_3$-$0.5\%K_2O$-ZrO_2	CO/H_2	9.6	19.5	25.6	27.8
	$CO_2/CO/H_2$	14.8	23.9	28.3	34.9
$8.6\%Y_2O_3$-ZrO_2	CO/H_2	4.0	18.6	24.2	26.1
	$CO_2/CO/H_2$	7.5	21.4	28.1	31.3

[a] Reaction conditions: 5.0 MPa, GHSV = 650 h^{-1}.
[b] CO/H_2 = 1/1.
[c] CO/H_2 = 1/1, CO_2: 5%.

could be also verified by comparing the H_2 conversions under $CO_2/CO/H_2$ atmosphere with that under CO/H_2. The H_2 conversions on ZrO_2 catalyst at different temperatures are shown in Table 2. It can be seen that the conversions of H_2 in the presence of 5% CO_2 in the feed were all higher than that without CO_2 present at all temperatures. In addition, the yields of hydrocarbons under the two different atmospheres were very similar, as shown in Fig. 1. Therefore, the much higher H_2 consumptions in the presence of CO_2 than without CO_2 present in the feed should be due to the enhancement of the rates of reverse WGS reaction because the reverse WGS reaction also consumed H_2. The inhibition effects of CO_2 on CO_2 formation were stronger at higher temperatures, as shown in Fig. 1. This could be due to the faster rates of forward WGS (formation of CO_2 and H_2 from CO/H_2O) and the less favorable equilibrium at higher temperatures.

It has been reported that methanol synthesis rates were promoted when small amounts of CO_2 (2–6%) were added to CO/H_2 mixtures [34,35]. In the synthesis of i-C_4 hydrocarbons from CO/H_2 (i.e., isosynthesis), surface methoxy (intermediate to methanol) has also been widely suggested as the C_1 intermediates to i-C_4 and other (C_{3+}) hydrocarbons (by aldol condensation), as observed by IR, and NMR, etc. [36–40]. Therefore, the introduction of small amounts of CO_2 would also promote the formation of surface methoxy species, and subsequently hydrocarbons on ZrO_2-based catalyst in the isosynthesis. This is evident in this study, as shown in Fig. 1. So the small losses of CO conversions in Fig. 1 with the addition of 5% CO_2 is merely attributed to the reduced conversions of CO to CO_2.

The selectivites to i-C_4 in total hydrocarbons on ZrO_2 catalyst from both reactant mixtures decreased with increasing temperature, as shown in Fig. 1. The presence of 5% CO_2 in the synthesis gas slightly decreased the i-C_4 hydrocarbons production, although the formation of hydrocarbons was slightly promoted by adding small amounts of CO_2, as indicated above. This could be due to that CO_2 present in the feed affected the catalyst during the reactions. Zirconia is well known as a bifunctional catalyst with both acidic and basic sites. The basic sites have been reported to be very significant for the formation of i-C_4 hydrocarbons in the isosynthesis reaction from CO/H_2 [5,6,10–12]. CO_2 is a weakly acidic gas

that has been widely employed as the molecule probe in the measurements of surface basic sites of solid catalysts by TPD. The added CO_2 could adsorb on the basic sites of ZrO_2 during the reactions, that results in less basic sites available for the formation of i-C_4 hydrocarbons. But the influences were very small with only 5% CO_2 present in the reaction system.

The experiments were repeated on $15.3\%Al_2O_3$-$0.5\%K_2O$-ZrO_2, and $8.6\%Y_2O_3$-ZrO_2 catalysts, and the results are presented in Figs. 2 and 3, respectively. Very similar effects of CO_2 addition on the catalytic performances have been observed in Figs. 2 and 3 on $15.3\%Al_2O_3$-$0.5\%K_2O$-ZrO_2 and $8.6\%Y_2O_3$-ZrO_2 catalysts as in Fig. 1 on ZrO_2 catalyst. The yields of CO_2 with 5% CO_2 adding in the feed were lower than that without CO_2 present on both catalysts, especially at higher temperatures. This can be also attributed to the increase of the rates of reverse WGS reaction with the addition of CO_2 in the feed. As shown in Table 2, the H_2 conversions on $15.3\%Al_2O_3$-$0.5\%K_2O$-ZrO_2 or $8.6\%Y_2O_3$-ZrO_2 catalyst under $CO_2/CO/H_2$ atmosphere were higher than that under CO/H_2 on the same catalyst. The inhibition effects of CO_2 adding in the feed on the formation of CO_2 were most remarkable on $8.6\%Y_2O_3$-ZrO_2
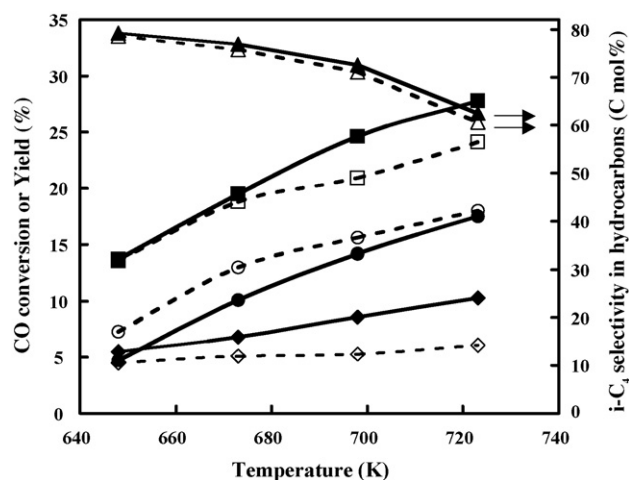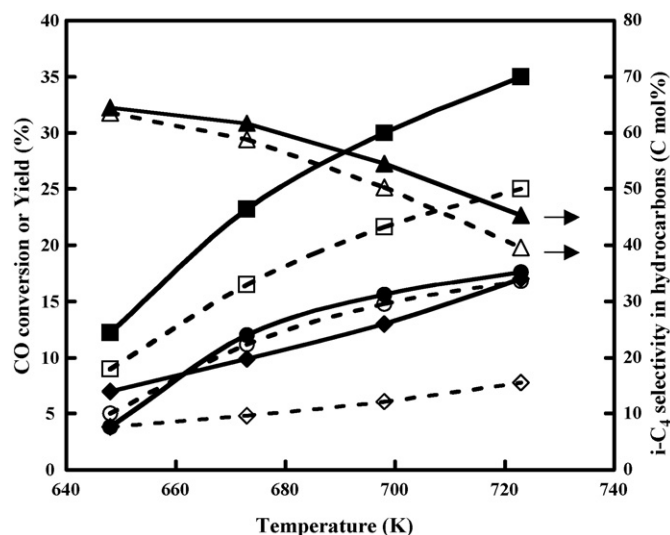

Fig. 2. CO conversion (■, □), yield of hydrocarbons (●, ○), CO_2 yield (◆, ◇), and i-C_4 selectivity in total hydrocarbons (▲, △) as a function of temperature on $15.3\%Al_2O_3$-$0.5\%K_2O$-ZrO_2 catalyst from CO/H_2 (filled symbols, CO/H_2 = 1/1) or $CO_2/CO/H_2$ (open symbols, CO/H_2 = 1/1, CO_2: 5%) at a total pressure of 5.0 MPa and 650 h^{-1}.

Fig. 3. CO conversion ($\blacksquare$, $\square$), yield of hydrocarbons ($\bullet$, $\bigcirc$), CO$_2$ yield ($\blacklozenge$, $\lozenge$), and i-C$_4$ selectivity in total hydrocarbons ($\blacktriangle$, $\triangle$) as a function of temperature on 8.6%Y$_2$O$_3$-ZrO$_2$ catalyst from CO/H$_2$ (filled symbols, CO/H$_2$ = 1/1) or CO$_2$/CO/H$_2$ (open symbols, CO/H$_2$ = 1/1, CO$_2$: 5%) at a total pressure of 5.0 MPa and 650 h^{-1}.

among three catalysts investigated. This may be attributed to the higher CO$_2$ formation rates on this catalyst where WGS and other CO$_2$ formation reactions were more close to equilibrium in comparison to both ZrO$_2$ and 15.3%Al$_2$O$_3$-0.5%K$_2$O-ZrO$_2$ catalysts [11,12]. As shown in Figs. 1–3 and Table 3, 8.6%Y$_2$O$_3$-ZrO$_2$ catalyst had the highest CO$_2$ selectivity and yields among the three catalysts from CO/H$_2$, that could be attributed to the stronger oxidization properties of 8.6%Y$_2$O$_3$-ZrO$_2$ (Table 1) because CO$_2$ can also form via oxidizing CO by surface oxygen (O*) [30]. The significant decreases in the formation of CO$_2$ during the reactions from CO$_2$/CO/H$_2$ on 8.6%Y$_2$O$_3$-ZrO$_2$ mainly account for the much lower CO conversions than that from CO/H$_2$ because the addition of 5% CO$_2$ only had very small effects on the formation of hydrocarbons, as shown in Fig. 3. The influences of CO$_2$ adding on the i-C$_4$ selectivities in total hydrocarbons over 8.6%Y$_2$O$_3$-ZrO$_2$ catalyst were larger than that over ZrO$_2$ and 15.3%Al$_2$O$_3$-0.5%K$_2$O-ZrO$_2$ catalysts. This could be due to the lowest basic sites quantity on 8.6%Y$_2$O$_3$-ZrO$_2$, as shown in Table 1.

Fig. 4. CO conversion ($\blacktriangle$), yield of hydrocarbons ($\square$), CO$_2$ yield ($\blacklozenge$), as a function of the content of CO$_2$ in the feed on ZrO$_2$ catalyst at 673 K, 5.0 MPa, 650 h^{-1}, CO/H$_2$ = 1/1.

The results presented in Figs. 1–3 indicate that the introduction of 5% CO$_2$ to the feed significantly reduced the net formation of CO$_2$, but the formation of hydrocarbons and the distribution of hydrocarbons were only slightly affected. Therefore, the i-C$_4$ selectivities in all products could be enhanced remarkably on the ZrO$_2$-based catalysts, as can be seen in Table 3.

3.3. Effects of the content of CO$_2$ in synthesis gas on isosynthesis

CO conversion and yields of hydrocarbons and CO$_2$ are shown as a function of the content of CO$_2$ added in the reactant mixtures on ZrO$_2$, 8.6%Y$_2$O$_3$-ZrO$_2$, and 15.3%Al$_2$O$_3$-0.5%K$_2$O-ZrO$_2$ catalysts in Figs. 4–6. The ratios of CO to H$_2$ were constant (1/1), and the system pressures were 5.0 MPa for all reactant mixtures. It can be seen that the CO conversions and yields of CO$_2$ sharply decreased with increasing CO$_2$ content in the feeds from 0 to 10%. The influences were much smaller when the CO$_2$ contents were further increased to 20% owing to the fact that the WGS reaction was significantly away from equilibrium with >10% CO$_2$ present in the feed. The

Table 3
Comparison of CO$_2$, and i-C$_4$ selectivities in the products from CO/H$_2$ and CO$_2$/CO/H$_2$ in the quartz-lined stainless-steel tubular reactor[a]

Catalyst	Feed gas	CO$_2$ selectivity in products (C mol%)	i-C$_4$ selectivity in products (C mol%)
ZrO$_2$	CO/H$_2$[b]	39.1	28.4
	CO$_2$/CO/H$_2$[c]	31.8	33.6
15.3%Al$_2$O$_3$-0.5%K$_2$O-ZrO$_2$	CO/H$_2$	34.8	39.8
	CO$_2$/CO/H$_2$	27.6	52.5
8.6%Y$_2$O$_3$-ZrO$_2$	CO/H$_2$	42.8	31.9
	CO$_2$/CO/H$_2$	29.3	39.9

[a] Reaction conditions: 673 K, 5.0 MPa, GHSV = 650 h^{-1}.
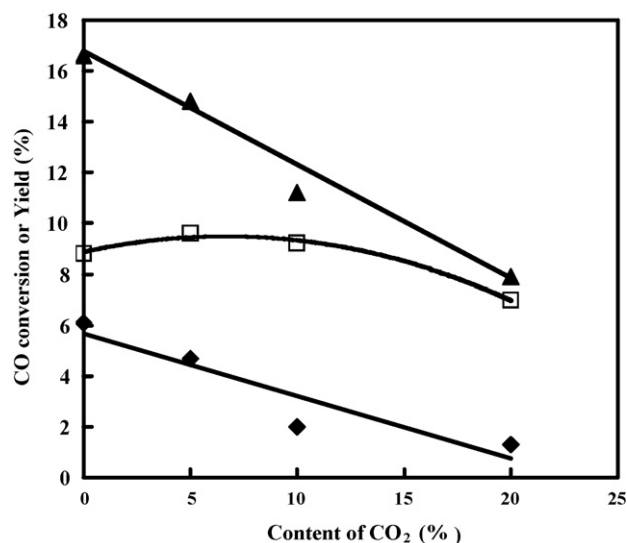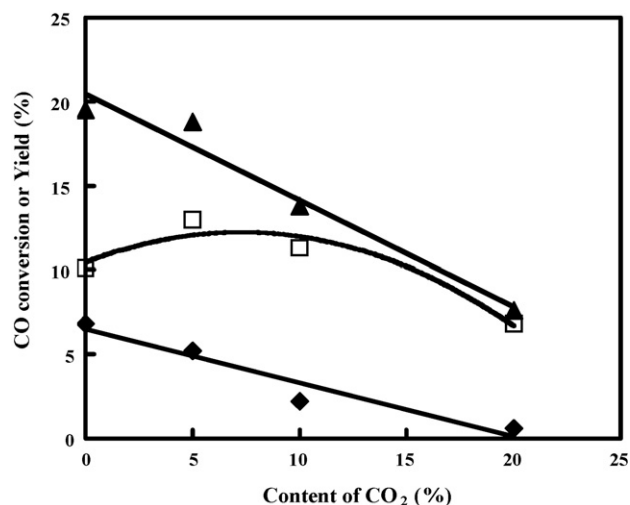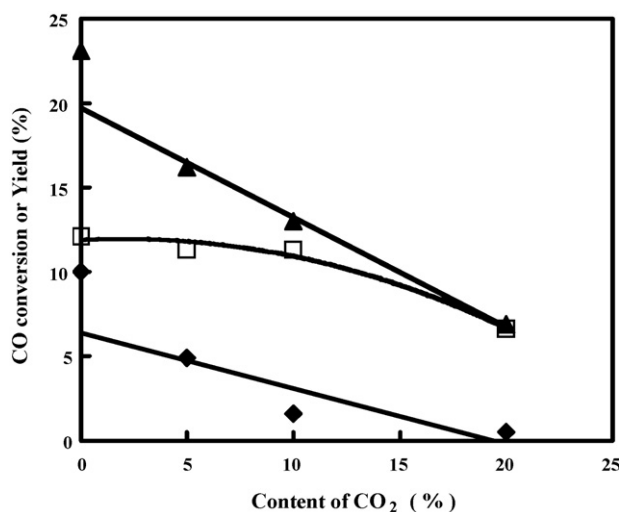[b] CO/H$_2$ = 1/1.
[c] CO/H$_2$ = 1/1, CO$_2$: 5%.

Fig. 5. CO conversion (▲), yield of hydrocarbons (□), CO_2 yield (◆), as a function of the content of CO_2 in the feed on 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst at 673 K, 5.0 MPa, 650 h^{-1}, CO/H_2 = 1/1.

Fig. 6. CO conversion (▲), yield of hydrocarbons (□), CO_2 yield (◆), as a function of the content of CO_2 in the feed on 8.6%Y_2O_3-ZrO_2 catalyst at 673 K, 5.0 MPa, 650 h^{-1}, CO/H_2 = 1/1.

Fig. 7. i-C_4 selectivity in hydrocarbons as a function of content of CO_2 in the feed at 673 K, 5.0 MPa, 650 h^{-1}, CO/H_2 = 1/1. (▲): ZrO_2, (■): 15.3%Al_2O_3-0.5%K_2O-ZrO_2, and (○): 8.6%Y_2O_3-ZrO_2.

yields of CO_2 were close to zero when the contents of CO_2 were 20%, especially on 8.6%Y_2O_3-ZrO_2, and 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalysts, indicating nearly complete inhibition of CO_2 formation. However, the formation of hydrocarbons was not affected when the concentrations of CO_2 in the reactant mixtures were lower than 10%. Therefore, the inhibition of the formation of CO_2 is the main cause for the decreases in CO conversions when the contents of CO_2 in the feeds were lower than 10%. With 20% CO_2 present in the feed, the yields of hydrocarbons decreased significantly. This is reasonable because the partial pressure of CO/H_2 dropped from the original 5.0 MPa to 4.0 MPa when CO_2 content was increased from 0 to 20% (at same total system pressures). Formation of hydrocarbons is more favorable at higher pressures because it is clear that hydrocarbons formation from CO and H_2 are the reactions that decrease the total numbers of molecules. In addition, the effects of CO_2 adding from the completive
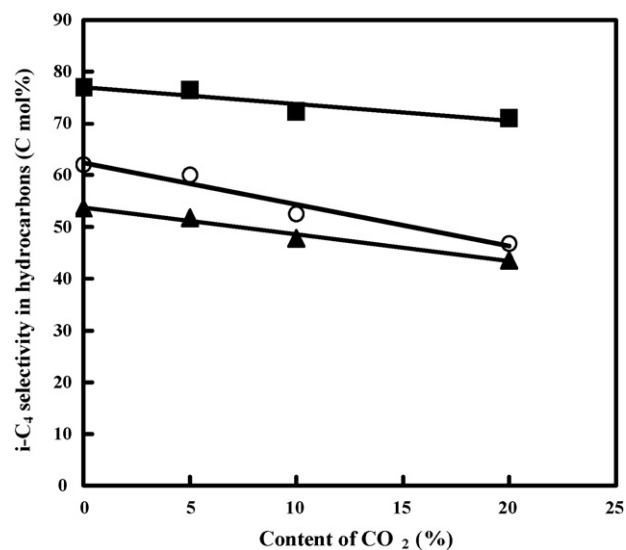
adsorption of CO_2 with CO would have been remarkable with so much CO_2 present in the feeds, although it is not noticeable at low CO_2 additions.

Fig. 7 shows the i-C_4 selectivities in total hydrocarbons as a function of CO_2 content in the reactant mixtures on ZrO_2, 8.6%Y_2O_3-ZrO_2, and 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalysts. The i-C_4 selectivities in hydrocarbons decreased with increasing the content of CO_2 in the feed. The slopes of the i-C_4 selectivity curves follow the order: 8.6%Y_2O_3-ZrO_2 > ZrO_2 > 15.3%Al_2O_3-0.5%K_2O-ZrO_2. On 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst, the i-C_4 selectivity was still higher than 70% when the concentration of CO_2 in the feed was 20%. From the previously published results on isosynthesis from CO/H_2, it could be concluded that the partial pressure of CO/H_2 was not the predominant factor in determining the i-C_4 selectivity in total hydrocarbons [6–22]. Maruya et al. also obtained very high i-C_4 selectivities (70–80%) even at pressures lower than 1 atm [22]. Therefore, the decreases in the i-C_4 selectivities in total hydrocarbons could not be attributed to the drops of CO/H_2 partial pressures in the reactant mixtures. As discussed above (Section 3.2), the possible adsorption of added CO_2 on the basic sites of the catalysts could account for the influences on the i-C_4 selectivity, especially with higher contents of CO_2 in the synthesis gas (CO/H_2). As shown in Table 1, the quantities of basic sites follow the order: 15.3%Al_2O_3-0.5%K_2O-ZrO_2 > ZrO_2 > 8.6%Y_2O_3-ZrO_2, that matches the order of the slopes of i-C_4 selectivity curves changing with CO_2 contents. Therefore, 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst can still keep higher i-C_4 selectivities from $CO_2/CO/H_2$ reactant mixture with 20% CO_2 present because of its higher quantity of surface basic sites. The acid–base and redox properties appear to be still the predominant factors in determining the catalytic performances of ZrO_2-based catalysts in the synthesis of i-C_4 from $CO_2/CO/H_2$, as have been widely suggested in the isosynthesis from CO/H_2 [6–22].
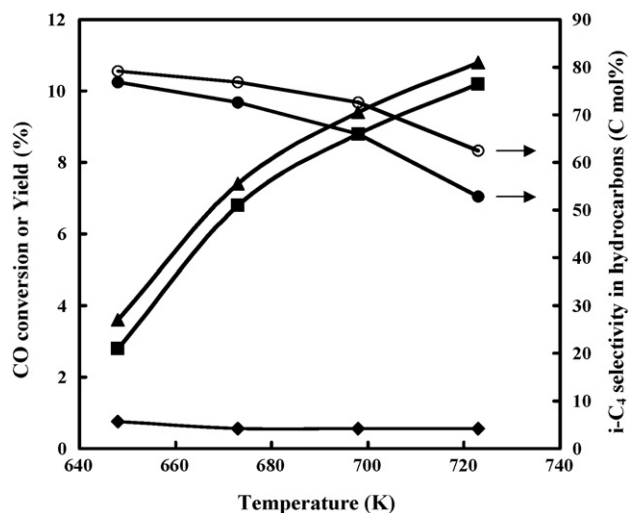
Fig. 8. CO conversion (▲), yield of hydrocarbons (■), CO_2 yield (◆), and i-C_4 selectivity in total hydrocarbons (●), as a function of temperature on 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst from CO_2/CO/H_2 (CO/H_2 = 1/1, CO_2: 20%) at a total pressure of 5.0 MPa and 650 h^{-1}. (○): i-C_4 selectivity in total hydrocarbons on 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst from CO/H_2 (CO/H_2 = 1/1) at 5.0 MPa and 650 h^{-1}.

Fig. 8 shows CO conversion, yields of hydrocarbons and CO_2, and i-C_4 selectivities in total hydrocarbons on 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst as a function of temperature with 20% CO_2 present in CO/H_2. It can be seen that CO conversions and yields of hydrocarbons increased with increasing temperatures. But the enhancement effects were weaker at higher temperatures. The yields of CO_2 were not affected by the temperatures, and the values were around 0.5%. The results indicated that the formation of CO_2 were almost completely inhibited on 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst with the addition of 20% CO_2 to the feed. The selectivities to i-C_4 in total hydrocarbons decreased with an increase in temperature. In addition, the effect of CO_2 on the i-C_4 selectivities in hydrocarbons was stronger at higher temperatures, as shown in Fig. 8. The i-C_4 selectivity in hydrocarbons decreased to about 50% when the temperature was increased to 723 K with 20% CO_2 present in the feed, and the selectivity to C_1–C_3 hydrocarbons has been increased to around 30%. At 698 K, the yield of hydrocarbons was 8–9% with ~65% i-C_4 selectivity in total hydrocarbons. Therefore, a 5–6% yield of i-C_4 hydrocarbons could be obtained with only 0.5% CO_2 yield (~5% CO_2 selectivity in the products).

The thermodynamics equation constant (K_p) for WGS reaction at 698 K is calculated to be around 8 by using the following equation:

$$K_p = \exp\left(\frac{-\Delta_r G}{RT}\right) \tag{1}$$

where $\Delta_r G$ is the Gibbs free energy for WGS reaction at different temperatures. If we assume that the concentration of H_2O in the system is 8%, i.e., there is 8% CO being converted into hydrocarbons and H_2O (without CO_2 production). The partial pressure of CO_2 required to fully inhibit the net formation of CO_2 in WGS

can be predicted from the following equation:

$$K_p = \frac{P_{CO_2} \times P_{H_2}}{P_{CO} \times P_{H_2O}} \tag{2}$$

where P_j is the partial pressure of j species. The P_{CO_2} is calculated to be ~0.64 from Eq. (2) if assuming $P_{CO} = 1$. That is, for the isosynthesis from 1/1 ratio of CO/H_2, the content of CO_2 in the feed must be around 24% in order to completely inhibit the net formation of CO_2 at 698 K.

From the above thermodynamic calculation results, it can be seen that the addition of 20% CO_2 in the feed could not fully inhibit CO_2 formation at 698 K. The predicted net formation of CO_2 during the reaction at 698 K with 20% CO_2 present in the feed would ~1% by using Eq. (2). Our experimental result showed that the yield of CO_2 was ~0.5% on 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst, as shown in Fig. 8. The two values match well. The small difference between the predicted value and the experimental result could be attributed to the influences of kinetics factors on 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst in the isosynthesis reaction.

3.4. CO_2 hydrogenation results

The catalytic performances of ZrO_2, 8.6%Y_2O_3-ZrO_2, and 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalysts in the hydrogenation of CO_2 (CO free) are summarized in Table 4. The reactions were carried out at 648–723 K, i.e., the same temperatures as that used in CO/H_2, and CO_2/CO/H_2 reactions (Figs. 1–8). It can be seen that all the catalysts were active in the conversion of CO_2. The conversion of CO_2 increased with increasing temperatures. CO and H_2O were the only two detectable products in these reactions. The absence of hydrocarbons, CH_3OH, and CH_3OCH_3, etc., indicates that ZrO_2, 8.6%Y_2O_3-ZrO_2, and

Table 4
CO_2 hydrogenation results in the quartz-lined stainless-steel tubular reactor[a]

Catalyst	T (K)	CO_2 conversion (%)	Selectivity (C mol%)[b]		
			CO[c]	CH[d]	CHO[e]
ZrO_2	648	11.0	100	–[f]	–
	673	17.9	100	–	–
	698	23.2	100	–	–
	723	26.1	100	–	–
15.3%Al_2O_3-0.5%K_2O-ZrO_2	648	18.5	100	–	–
	673	22.4	100	–	–
	698	26.3	100	–	–
	723	29.8	100	–	–
8.6%Y_2O_3-ZrO_2	648	6.5	100	–	–
	673	13.3	100	–	–
	698	20.8	100	–	–
	723	23.6	100	–	–

[a] Reaction conditions: CO_2/H_2 = 1/1, 5.0 MPa, 650 h^{-1}.
[b] Selectivity in the products containing carbon atoms.
[c] Based on the net CO formation in the reaction.
[d] Hydrocarbons.
[e] CH_3OH + CH_3OCH_3.
[f] Not detected.

15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalysts cannot convert CO_2 and H_2 into these products. The typical catalysts that are active for CO_2 hydrogenation to produce hydrocarbons, or CH_3OH are Fe-Co or Cu-Zn catalysts, etc. [41–43]. These results suggest that reverse WGS reaction was the predominant reaction under the reaction conditions in this study. If the WGS reaction is at equilibrium at 698 K, the predicted conversion of CO_2 by thermodynamics calculation is ∼26%. It can be seen from Table 4 that the conversions of CO_2 on the catalysts at 698 K varied from 20 to 26.3% following the order: 15.3%Al_2O_3-0.5%K_2O-ZrO_2 > ZrO_2 > 8.6%Y_2O_3-ZrO_2. The results are reasonable if the adsorption abilities of CO_2 on these catalysts are considered, as measured by CO_2-TPD.

It can be summarized from the above results that the additions of CO_2 in the feed could remarkably suppress the formation of CO_2, but did not affect the formation of hydrocarbons significantly, especially when CO_2 adding amounts were lower than 10%. Our results are in agreement with the data of the effects of CO_2 addition on F-T synthesis from CO/H_2 over iron-based catalysts reported by Krishnamoorthy et al. [30]. The roles of CO_2 in the feed (CO/H_2) were mainly to increase the reverse CO_2 formation rates but not affect the rates of their forward steps leading to the attainment of WGS equilibrium [30]. In addition, CO_2 did not participate in the chain initiation and growth reactions to hydrocarbons on the ZrO_2-based isosynthesis catalysts under the typical isosynthesis reaction temperatures (648–723 K), as shown in Table 4. Our results can be supported by the isotopic results of Hall et al. [44]. They found that the addition of $^{14}CO_2$ to $^{12}CO/H_2$ (1:1) did not lead to detectable ^{14}C contents in hydrocarbons on Fe catalysts. However, Xu and co-workers detected almost identical radioactivity per mole in CO_2 and in hydrocarbons on an Fe-Si-K catalyst [45,46]. These latter results are surprising because CO and CO_2 become kinetically indistinguishable when WGS reactions approach equilibrium during F-T synthesis on Fe-based catalysts. The chemical (and isotopic) interconversion between CO and CO_2 that is much faster than the chain initiation and growth steps for hydrocarbon formation would render a significant fraction of the ^{14}C atoms in $^{14}CO_2$ towards the formation of hydrocarbons via the formation of ^{14}CO intermediates from reverse WGS reactions.

The obtained results suggest that it would be possible to use the recycle of CO_2 formed during the isosynthesis reaction to improve the carbon efficiency on ZrO_2-based catalysts in potential industrial applications, as shown in Fig. 9. The recycling gas mixtures (R) contain mainly $CO/H_2/CO_2$, and also small amounts of C_1–C_3 hydrocarbons after separating the C_{4+} hydrocarbons and H_2O by condensation from the products. The ratio Q (Q = R/F) of freshly added CO/H_2 feed (F) to recycle gas (R) can be set to maintain a stable state of the reaction system. The ratio Q can be calculated by using the known thermodynamics data and the mass balances for a definite reaction system. Here we take 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst as an example. The system temperature, and pressure are 698 K, and 5.0 MPa, respectively. From the obtained experimental data and calculation results in Section 3.3, assuming 8% conversion of CO on the catalyst, we have
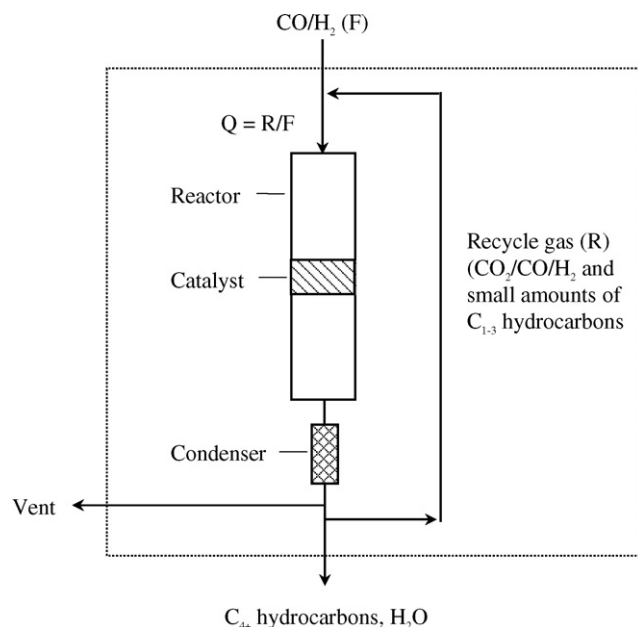

Fig. 9. Potential use of CO_2 recycle in industrial application on synthesis of i-C_4 hydrocarbons from coal or natural gas derived syn-gas (CO/H_2).

known that there will be no net formation of CO_2 when the content of CO_2 in the reactor system approach ∼24% ($CO/H_2/CO_2$ = 1/1/0.64). The obtained experimental results on 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst indicated that alkenes were the predominant products (80–90%). Therefore, the ratio of consumption quantity of CO to that of H_2 could be considered to be about 1:2. If taking the quantity of CO in the reactant mixtures (R + F) before entering the reactor as 1 U volume, the total volumes of C_{4+} and H_2O will be about 0.15 U volume at 8% CO conversion from $CO/H_2/CO_2$ (1/1/0.64). After removing the condensed products (C_{4+} and H_2O), the concentration of CO_2 in the recycling gas mixtures will be around 26.6% ($CO/H_2/CO_2$ = 0.92/0.84/0.64). Prior to entering the reactor again, the content of CO_2 can be adjusted back to ∼24% by adding fresh CO/H_2 feed (F) into the recycles (R). Here the amount of the freshly added CO/H_2 is nearly 0.24 U volume, i.e., one tenth of that of the recycles (2.4 U volume in total). The ratio of CO to H_2 in the recycle gas mixtures (R) might not be 1:1, but it can be adjusted back to 1:1 by altering the ratio of CO to H_2 in the freshly added feed (F). Because the content of CO_2 in the reactant mixture is ∼24%, the conversion of CO would be slightly lower than that obtained in present study (Fig. 8) on 15.3%Al_2O_3-0.5%K_2O-ZrO_2 catalyst at 5.0 MPa with 20% CO_2 present (i.e., 8–9%). But it should be able to be achieved by a little increase of the reactor pressure. In addition, the presence of small amounts of C_1–C_3 hydrocarbons in the reactant mixtures would not affect the conversion of CO. But it should be noted that C_1–C_3 hydrocarbons could be accumulated with recycling times. The concentration of C_1–C_3 hydrocarbons could be controlled by suitable venting. Another possibility is that the formation of C_1–C_3 hydrocarbons could be inhibited when the content of C_1–C_3 hydrocarbons in the reactant mixture has been accumulated to be enough to affect the reactions towards C_1–C_3 hydrocarbons. If this were true, venting would be unnecessary.

Therefore, the recycle of CO_2 formed during the isosynthesis reaction to improve the carbon efficiency (without CO_2 formation) could be practical from the theoretical calculations. The formation of CO_2 is completely inhibited with ~62% of consumed CO being converted into i-C_4 hydrocarbons at 698 K. The one-pass yield of i-C_4 hydrocarbons is 5–6% at 5.0 MPa. It can be anticipated that further increases in i-C_4 hydrocarbons yields can be expected, with higher reaction pressures, and exploring more active and selective catalysts (with appropriate acid–base and redox properties [12]) in the isosynthesis.

4. Conclusions

In conclusion, we have shown that synthesis of i-C_4 hydrocarbons from CO_2/CO/H_2 reactant mixtures on ZrO_2-based catalysts could be a very promising way for highly selective production of i-C_4 hydrocarbons. The presence of CO_2 in the feed (CO/H_2) affected the net formation of CO_2, but did not influence the formation quantities of hydrocarbons remarkably. Therefore, the i-C_4 selectivities in the products could be enhanced significantly, which were substantially higher than that obtained in the traditional isosynthesis from merely CO/H_2. CO_2 did not participate in the chain initiation and growth reactions towards hydrocarbons on ZrO_2-based catalysts at the typical isosynthesis reaction temperatures (648–723 K). The decrease in CO conversion with CO_2 present in the feed was mainly due to the less formation of CO_2 during the reactions. However, the distribution of hydrocarbon products could be influenced, especially at higher temperatures and higher CO_2 contents in the feed. This could be attributed to the occupancies of more and more basic sites on ZrO_2-based catalysts by CO_2 molecules with increasing the amount of CO_2 added. From our experimental data and thermodynamic calculation results, it was found that at 698 K, the addition of ~24% CO_2 to synthesis gas (CO/H_2 = 1, 5.0 MPa) could completely eliminate CO_2 formation during isosynthesis. These results suggest that it could be potential to use the recycle of CO_2 formed during the isosynthesis reaction to improve the carbon efficiency in future industrial applications. The catalysts with appropriate acid–base and redox properties will have excellent catalytic performances in the synthesis of i-C_4 from CO_2/CO/H_2.

References

[1] A. Sofianos, Catal. Today 15 (1992) 149–175.
[2] H. Pichler, K.H. Ziesecke, Brennst. Chem. 30 (1949) 13–22.
[3] H. Pichler, K.H. Ziesecke, Brennst. Chem. 30 (1949) 60–68.
[4] T. Maehashi, K. Maruya, K. Domen, K. Aika, T. Onishi, Chem. Lett. (1984) 747–748.
[5] K. Maruya, T. Maehashi, T. Haraoka, S. Narui, Y. Asakawa, K. Domen, T. Onishi, Bull. Chem. Soc. Jpn. 61 (1988) 667–671.
[6] Z.T. Feng, W.S. Postula, A. Akgerman, R.G. Anthony, Ind. Eng. Chem. Res. 34 (1995) 78–82.
[7] N.B. Jackson, J.G. Ekerdt, J. Catal. 126 (1990) 31–45.
[8] C.L. Su, J.R. Li, D.H. He, Z.X. Cheng, Q.M. Zhu, Appl. Catal. A 202 (2000) 81–89.
[9] C.L. Su, D.H. He, J.R. Li, Z.X. Cheng, Q.M. Zhu, J. Mol. Catal. 153 (2000) 139–146.
[10] Y.W. Li, D.H. He, Z.X. Cheng, C.L. Su, J.R. Li, Q.M. Zhu, J. Mol. Catal. 175 (2001) 267–275.
[11] Y.W. Li, D.H. He, Y.B. Yuan, Z.X. Cheng, Q.M. Zhu, Energy Fuels 15 (2001) 1434–1440.
[12] Y.W. Li, D.H. He, Q.M. Zhu, X. Zhang, B.Q. Xu, J. Catal. 221 (2004) 584–593.
[13] R. Kieffer, J. Varela, A. Deluzarche, J. Chem. Soc. Chem. Commun. (1983) 763–764.
[14] W.S. Postula, Z.T. Feng, C.V. Philip, R.G. Anthony, J. Catal. 145 (1994) 126–131.
[15] Z.T. Feng, W.S. Postula, C. Erkey, C.V. Philip, R.G. Anthony, J. Catal. 148 (1994) 84–90.
[16] W.S. Postula, R.G. Anthony, Appl. Catal. A 112 (1994) 175–185.
[17] S.C. Tseng, N.B. Jackson, J.G. Ekerdt, J. Catal. 109 (1990) 284–297.
[18] K. Maruya, T. Fujisawa, A. Takasawa, K. Domen, T. Onishhi, Bull. Chem. Soc. Jpn. 62 (1989) 11–16.
[19] M. Hara, M. Kawamura, K. Maruya, Chem. Lett. 26 (1997) 309–310.
[20] L.H. Lu, T. Hayakawa, T. Ueda, K. Domen, M. Hara, K. Maruya, Chem. Lett. 27 (1998) 65–67.
[21] K. Maruya, T. Komiya, K. Okumura, M. Yashima, Chem. Lett. 28 (1999) 575–576.
[22] K. Maruya, T. Komiya, T. Hayakawa, L.H. Lu, M. Yashima, J. Mol. Catal. A 159 (2000) 97–102.
[23] T. Inui, M. Anpo, K. Izui, S. Yanagida, T. Yamaguchi (Eds.), Advances in chemical conversions for mitigating carbon dioxide, Stud. Surf. Sci. Catal., vol. 114, Elsevier, Amsterdam, 1998, pp. 1–20.
[24] D.S. Newsome, Catal. Rev. Sci. Eng. 21 (1980) 275–318.
[25] Y.W. Li, D.H. He, Q.J. Zhang, B.Q. Xu, Q.M. Zhu, Fuel Process. Technol. 85 (2004) 401–411.
[26] S.L. Soled, E. Iglesia, S. miseo, B.A. DeRites, R.A. Fiato, Topics Catal. 2 (1995) 193–205.
[27] M. Sahibzada, I.S. Metcalfe, D. Chadwick, J. Catal. 174 (1998) 111–118.
[28] A. Hilmen, M. Xu, M.J.L. Gines, E. Iglesia, Appl. Catal. A 169 (1998) 355–372.
[29] T. Riedel, M. Claeys, H. Schulz, G. Schaub, S. Nam, K. Jun, M. Choi, G. Kishan, K. Lee, Appl. Catal. A 186 (1999) 201–213.
[30] S. Krishnamoorthy, A. Li, E. Iglesia, Catal. Lett. 80 (2002) 77–86.
[31] R.B. Anderson, K. Friedel, H. Storch, J. Chem. Phys. 19 (1951) 313–319.
[32] B.Q. Xu, T. Yamaguchi, K. Tanabe, Chem. Lett. (1988) 1663–1666.
[33] R.G. Silver, C.J. Hou, J.G. Ekerdt, J. Catal. 118 (1989) 400–416.
[34] G.A. Vedage, P.B. Himelfarb, G.W. Simmons, K. Klier, ACS Symp. Ser. 279 (1985) 295–296.
[35] K. Klier, V. Chatikavanij, R.G. Herman, G.W. Simmons, J. Catal. 74 (1982) 343–360.
[36] T.J. Mazanec, J. Catal. 98 (1986) 115–125.
[37] J.G. Nunan, C.E. Bogdan, K. Klier, K.J. Smith, C.W. Young, R.G. Herman, J. Catal. 116 (1989) 195–221.
[38] H. Abe, K. Maruya, K. Domen, T. Onishi, Chem. Lett. 13 (1984) 1875–1877.
[39] K. Maruya, A. Takasawa, M. Alkawa, T. Haraoka, K. Domen, T. Onishi, J. Chem. Soc. Faraday Trans. 90 (1994) 911–917.
[40] K. Maruya, A. Takasawa, T. Haraoka, K. Domen, T. Onishi, J. Mol. Catal. A 112 (1996) 143–151.
[41] F. Tihay, A.C. Roger, G. Pourroy, A. Kiennemann, Energy Fuels 16 (2002) 1271–1276.
[42] Y. Borodko, G.A. Somorjai, Appl. Catal. A 186 (1999) 355–362.
[43] Y. Choi, K. Futagami, T. Fujitani, J. Nakamura, Catal. Lett. 73 (2001) 27–31.
[44] W.K. Hall, R.J. Kokes, P.J. Emmett, J. Am. Chem. Soc. 79 (1957) 2983–2985.
[45] B.H. Davis, L.G. Xu, S.Q. Bao, Stud. Surf. Sci. Catal. 107 (1997) 175–180.
[46] L.G. Xu, S. Bao, D.J. Houpt, S.H. Lambert, B.H. Davis, Catal. Today 36 (1997) 347–355.